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SAMPLE TYPE VII(WATER-OXYGEN DEMAND)

Robert A. Taft Sanitary Engineering Center,
Cincinnati, Ohio

July 1960

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**SAMPLE TYPE VII
WATER-OXYGEN DEMAND
JULY, 1960**

analytical reference service

**T R A I N I N G
P R O G R A M**

Robert A. Taft

**SANITARY
ENGINEERING
CENTER**

**U. S. DEPARTMENT OF
HEALTH, EDUCATION,
AND WELFARE
PUBLIC HEALTH SERVICE
CINCINNATI, OHIO**

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ANALYTICAL REFERENCE SERVICE

SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

**Report of a laboratory performance study conducted
jointly with the participating member organizations.**

**Prepared by the
Analytical Reference Service
TRAINING PROGRAM**

**U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of State Services
Division of Engineering Services**

**Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio**

1960

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FOREWORD

The Analytical Reference Service is a voluntary association of organizations responsible for the conduct of laboratory programs. It is conducted by the Training Program of the Robert A. Taft Sanitary Engineering Center for the evaluation of laboratory methods in the field of sanitary engineering. Evaluations are obtained by the cooperative efforts of the member organizations in analysis of identical samples. This cooperative mechanism provides:

1. Statistical evaluation of procedures, including precision and accuracy.
2. Opportunity for comparison of laboratory procedures and results between laboratories having similar responsibilities.
3. Exchange of information regarding weaknesses of currently approved methods.
4. Evidence of the need for further development of methods or for entirely new approaches.
5. A framework for broad-scale evaluation of new analytical methods.

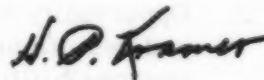
Initially the program was directed toward examination of water. It has been broadened to include other types of examinations and other media.

Using the most refined grade of chemicals available, samples are designed and prepared containing measured amounts of the desired constituents. Decisions as to qualitative makeup are made by the staff of ARS and the Center. Notice of sample availability and qualitative makeup is then sent to all member organizations.

Foreword

Immediately on receipt of the indication of willingness to participate, a portion of the sample is shipped with accompanying data forms which provide space for numerical values and a narrative critique of the analytical procedures used. The laboratories are urged to comment on the methods, including difficulties, modifications, sources of error, and other factors. Results are requested usually within sixty days.

These results, including the comments, are compiled as in the accompanying report. Examination of the data, it is hoped, will produce reliable estimates of the accuracy and precision of the methods employed.



H. P. Kramer
Chief, Training Program

ANALYTICAL REFERENCE SERVICE MEMBERS*

State Agencies

Alabama Water Improvement Commission
Arizona State Department of Health
Arkansas State Board of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health (Jacksonville)
Florida State Board of Health (Pensacola)
Florida State Board of Health (Winter Haven)
State of Hawaii Department of Health
Idaho State Board of Health
Illinois State Department of Public Health (Chicago)
Illinois State Department of Public Health (Springfield)
Illinois State Water Survey Division
Indiana State Board of Health
Kentucky State Department of Health
Louisiana State Health Department
Maryland State Department of Health
Maryland State Water Pollution Control Commission
Michigan State Department of Health
Minnesota State Department of Health
Missouri Department of Public Health & Welfare
Montana State Board of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey Department of Health
New Mexico State Department of Public Health
New York State Department of Health
New York State Conservation Department
North Carolina State Board of Health
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health

*July 1, 1960

State of Rhode Island and Providence Plantations
South Carolina Water Pollution Control Authority
South Dakota Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont State Department of Health
Vermont State Water Conservation Board
Virginia State Health Department
Virginia State Water Control Board
Washington State Department of Health
West Virginia State Water Commission
Wisconsin State Board of Health

Municipal Agencies

Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Los Angeles County Flood Control District
Chicago Department of Water and Sewers
Flint Department of Public Works and Utilities
Dayton Department of Service and Buildings
Philadelphia Suburban Water Co.
Philadelphia Water Quality Control and Research Division
St. Louis County Water Co.

Federal Agencies

Tennessee Valley Authority, Wilson Dam, Alabama (Lab I)
Tennessee Valley Authority, Wilson Dam, Alabama (Lab II)
Tennessee Valley Authority, Chattanooga, Tennessee
U. S. Army Environmental Health Laboratory, Md.
Sanitary Engineering Division, 13th Naval District, Seattle, Wash.
U. S. Dept. of the Interior, Geological Survey, Sacramento, Calif.
U. S. Dept. of the Interior, Geological Survey, Denver, Colorado
U. S. Dept. of the Interior, Bureau of Reclamation, Denver, Col.
U. S. Dept. of the Interior, Geological Survey, Columbus, Ohio
U. S. Dept. of the Interior, Geological Survey, Philadelphia, Pa.
U. S. Dept. of the Interior, Geological Survey, Washington, D. C.

Universities

Georgia Institute of Technology, Dept. of Applied Biology
Purdue University, Department of Chemistry
Rutgers University, Department of Sanitation
Case Institute of Technology, Dept. of Civil and Sanitary Engineering
University of Pittsburgh, Graduate School of Public Health

Industry

American Cyanamid Company
California Water Service Company (San Jose)
Central Farmers Fertilizer Company
Dearborn Chemical Company
Ekroth Laboratories, Inc.
Food Machinery & Chemical Corp.
Goodyear Atomic Corporation
Industrial Chemicals, Inc.
Monsanto Chemical Company
National Aluminate Corporation
Reynolds Electrical & Engineering Co., Inc.
Sandia Corporation

Foreign

Vancouver, B. C., Department of National Health & Welfare
Ottawa, Ontario, Department of National Health & Welfare

PARTICIPANTS IN THIS STUDY

Alabama Water Improvement Commission
Arizona State Department of Health
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
California Department of Water Resources
Colorado State Department of Public Health
Connecticut State Department of Health
Idaho State Board of Health
Kentucky State Department of Health
Louisiana State Health Department
Michigan State Department of Health
Minnesota State Department of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey Department of Health
New York State Department of Health
New York State Conservation Department
North Carolina State Board of Health
Ohio State Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
State of Rhode Island and Providence Plantations
South Carolina Water Pollution Control Authority
Tennessee Stream Pollution Control Board
Utah State Department of Health
Vermont State Water Conservation Board
Metropolitan Water District of Southern California
Los Angeles Department of Water and Power
Tennessee Valley Authority, Chattanooga, Tennessee
U. S. Army Environmental Health Laboratory, Md.
Georgia Institute of Technology, Dept. of Applied Biology
University of Pittsburgh, Graduate School of Public Health
American Cyanamid Company
Vancouver, B. C., Department of National Health & Welfare

SAMPLES ON WHICH REPORTS HAVE BEEN COMPLETED

SAMPLE TYPE I AND I-A

(Mineral, Water) analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

SAMPLE TYPE II

(Heavy Metals, Water) analyzed for copper, cadmium, aluminum, chromium, iron, manganese, and zinc.

SAMPLE TYPE III

(Fluoride, Water) analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLE TYPE IV

(Inorganics, Air) analyzed for chloride, sulfate, fluoride and nitrate in aqueous solution and on glass fiber hi-vol filter mats.

SAMPLE TYPE V

(Radiological, Water) analyzed for gross beta activity.

SAMPLE TYPE VI

(Water, Surfactant) analyzed for surfactant in various waters.

SAMPLES NOW UNDER STUDY

SAMPLE TYPE III-B

(Fluoride, Water) to be analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLE TYPE V-B

(Radiological, Water) to be analyzed for gross beta activity.

SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

PURPOSE OF THE STUDY

Biochemical Oxygen Demand has been used for many years as a parameter in the study of water pollution. It is useful in the design and operation of waste treatment facilities, in the evaluation of the effects of wastes on streams, and in the determination of water quality. In the past, many authorities have considered it the most important single parameter available.

In spite of the widespread use of this operational procedure, very little has been reported on the precision and accuracy of the determination as currently used. Evaluations appearing in the literature generally reported the measurement of reproducibility within a single laboratory, rather than a cooperative study by a group of laboratories. Among the reasons for the lack of specific information on the BOD determination are the following: (1) the procedure is essentially a bio-assay and therefore subject to wide biological variability, and (2) satisfactory samples are difficult to prepare and distribute.

Similarly, the Chemical Oxygen Demand determination, while not as widely applied as the BOD, is also an important parameter of oxidizability. Although a chemical determination, it involves a degree of variability that is related to the sample composition as well as to the precision and accuracy of the chemical measurement. To our knowledge the method has not been tested by a large group of laboratories working on the same sample.

This particular study was undertaken by the Analytical Reference Service in an attempt to fill the gaps in the available information on the precision and accuracy of these important oxygen demand determinations. Through simultaneous analysis of an identical sample, it is hoped that the common variables of the methods can be evaluated.

COMPOSITION OF SAMPLE AND ANALYSIS SCHEME

Sample Type VII consisted of a mixture of concentrated solutions of glucose and glutamic acid. The mixture contained 1.5 mg glucose and 1.5 mg glutamic acid per ml. Instructions accompanying the sample specified that the analyst prepare a 1:10 dilution of the sample for use in the BOD and COD determinations. When thus prepared the sample contained 150 mg/l of

Sample Type VII (Water, Oxygen Demand)

glucose and 150 mg/l glutamic acid. One percent and two percent dilutions of the BOD sample were to be prepared, using the synthetic dilution water specified in Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, Tenth edition, page 262. The samples were seeded with domestic sewage which had been filtered through glass wool or cotton and stored overnight at room temperature. Sufficient replicate bottles were prepared to permit measurement of the oxygen depletion at 2, 3, 5, and 7 days. Correction for the seed depletion was made by using a seed correction series. Precautions observed were: (1) incubation in the dark at 20°C, (2) close control of time intervals, (3) use of azide modification of the Winkler method for DO, and (4) careful selection of seed.

The COD of the sample was determined by the dichromate reflux procedure, Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, Tenth edition, page 333, using a 50 ml sample and silver sulfate catalyst.

TREATMENT OF THE DATA

In previous Analytical Reference Service studies, carefully weighed quantities of pure chemicals were added to deionized distilled water, so that analytical results could be judged in terms of deviation from the amount of chemical entity actually added to the sample. Similarly, in the preparation of Sample Type VII, carefully weighed amounts of the chemicals were added. In the analysis of this sample, however, results were reported in terms of the oxygen demand created by the materials, rather than the concentration of chemical substance in the sample. Since the biochemical oxygen demand is the result of biological activity, absolute values cannot be established. In this study, the correct BOD is assumed to be the result most frequently obtained by the laboratories participating. The data are arrayed in order of increasing value and the geometric mean, median and geometric standard deviation are reported. In the bar charts, the geometric mean is the central value. Throughout this report all values are in mg/l and no reported result was discarded.

Thirty-four agencies contributed data on Sample Type VII. Not all performed the entire set of determinations, so the number of results in each section may vary somewhat. In every case, however, sufficient results were reported to permit good statistical evaluation.

Sample Type VII (Water, Oxygen Demand)

PRECISION OF BOD

As stated previously, no absolute value can be established for the BOD determination. It is necessary, therefore, to confine the statistical discussion of the results to measures of precision. Examination of the data reveals that a log normal distribution exists for all dilutions, at all time intervals. This conclusion is substantiated by the appearance of the bar charts, Figs. 1 to 8 and the close agreement of the mean and median of all sets of data, Tables VII through X. A comparison of geometric mean values follows:

Table I. EFFECT OF SAMPLE CONCENTRATION ON BOD

Days incubated	Geo. mean BOD for 1% dilution	Geo. mean BOD for 2% dilution
2	120	119
3	152	154
5	187	184
7	207	196

These figures show that there was no significant difference in the mean value obtained from the two test concentrations. This result was to be expected, since these dilutions were selected to give depletions that would yield a satisfactory titration.

The geometric standard deviations show a slightly better precision for the 2% dilution, but the difference is so small as to be almost negligible.

Table II. PRECISION OF BOD RESULTS FOR DIFFERENT DILUTIONS AND INCUBATION PERIODS

Days incubated	Geometric standard deviation 1% dilution	Geometric standard deviation 2% dilution
2	± 35 (29%)	± 31 (26%)
3	± 31 (20%)	± 23 (15%)
5	± 41 (22%)	± 31 (17%)
7	± 52 (25%)	± 37 (19%)
Average precision	24%	19%

Sample Type VII (Water, Oxygen Demand)

The standard deviations shown in Table II can be interpreted as representing the range of values obtained by a majority (68%) of the reporting laboratories. The percentages, therefore, are the expected limits of precision for the BOD test. From a study of these values, it is evident that a precision of approximately $\pm 20\%$ can be expected from the test.

Many authorities believe that incubation periods shorter than the traditional five days result in erratic BOD values. This is assumed to be due to differences in the rate at which the organisms begin active utilization of the food material. This opinion, however, is not supported by the figures presented in Table II. The precision at the shorter incubation periods is not significantly different than that for the 5 day incubation. This result is undoubtedly due to the nature of the sample. The carbohydrate and amino acid used are readily available for oxidation, without a significant lag. Obviously, materials encountered in actual waste samples would not necessarily exhibit this same behavior.

SEEDING

In this study aliquots of a parent sample were examined, the laboratory procedures used were identical in every case, and the only important variable was the seed material. It is necessary, therefore, to examine the data in terms of the effect of the differences in sewage seed. In Table III the 5 day BOD of the seed used by each laboratory is shown, along with the average of the sample 5 day BOD reported by each laboratory. The seed BOD values are arrayed in order of increasing value, and the data are arbitrarily divided into four groups, representing four ranges of seed BOD. The mean of the seed BOD for each group has been calculated and compared with the mean of the sample BOD values obtained by the group.

Table III EFFECT OF SEED STRENGTH ON SAMPLE BOD

Lab. no.	Seed BOD	Sample BOD*	Arithmetic means
GROUP I			
20	4	133	
13	9	204	
23	12	215	
35	22	259	
19	27	116	
32C	45	230	
18	52	194	
4	71	255	
			seed: 30
			sample: 201

Sample Type VII (Water, Oxygen Demand)

Table III.EFFECT OF SEED STRENGTH ON SAMPLE BOD

Lab. no.	Seed BOD	Sample BOD*	Arithmetic means
GROUP II			
11	74	158	
26	82	216	
7	83	177	
25A	99	188	
34	99	151	
6	100	240	
28	107	218	seed: 94
32B	108	215	sample: 193
GROUP III			
15	114	131	
25B	114	216	
1	115	175	
29	130	163	
21	135	194	
3	142	217	
14	143	193	seed: 131
33	154	173	sample: 183
GROUP IV			
17	155	179	
22	164	174	
24	175	201	
9	180	204	
12	195	120	
2	198	202	
10	207	134	
8	213	194	seed: 196
5	277	206	sample: 178

*Average of both 1% and 2% dilution

The sample means in the right hand column of Table III are essentially in agreement, within the experimental of the error of the test. That is, there is no significant difference in the sample mean, attributable to the difference in the seed used. This conclusion is substantiated by the data in Table IV, where the seed corrections used in computing the BOD of the sample have been

Sample Type VII (Water, Oxygen Demand)

arrayed into groups of similar values. Particularly striking is the evidence that seed corrections below 0.6 mg/l were not accompanied by significantly different sample BOD values. These data suggest the need for more research into application of sewage as seed for sterile samples.

Table IV. SEED CORRECTION vs. 5-DAY BOD

Correction, mg/l	<0.2	0.2 - 0.4	0.4 - 0.6	>0.6
Median of all values 1% dilution	196	225	196	198
Median of all values 2% dilution	191	204	192	192
No. labs. reporting	3	6	5	22

OXIDATION RATE CONSTANT AND ULTIMATE BOD VALUES

Participants were requested to determine the BOD of the sample after 2, 3, 5, and 7 days of incubation. The curves shown in Figs. 9 and 10 were plotted using the geometric mean BOD values for the incubation periods specified. The Moments method of Moore, Thomas, and Snow was used to calculate the velocity constant "k" and the ultimate BOD "L". These values are shown in the following table:

Table V. VELOCITY CONSTANT k AND ULTIMATE DEMAND L

	1% Dilution	2% Dilution
k	0.18	0.18
L	215	212
Theoretical oxygen demand	308	308

Sample Type VII (Water, Oxygen Demand)

As a further check of the velocity rate constant, the individual results were used to obtain the "k" values shown in Table VI. Only those reports showing BOD values for all of the requested time intervals were used.

Table VI. VELOCITY CONSTANTS

Lab. no.	k
36	0.10
6	0.11
8	0.12
18	0.12
4	0.13
35	0.13
5	0.14
33	0.16
34	0.16
9	0.16
17	0.17
2	0.18
32C	0.20
25A	0.21
10	0.22
16	0.22
23	0.22
3	0.23
13	0.24
1	0.26
32B	0.27
Mean 0.18	

The rate constant "k" is quite close to that reported by Ruchoft for domestic sewage, but not as high as might be anticipated from the nature of the sample materials.

Sample Type VII (Water, Oxygen Demand)

The ultimate demand "L", when compared to the theoretical oxygen demand (assuming complete oxidation) indicates that this particular synthetic waste material exerts approximately 70% of the oxygen demand theoretically possible under the conditions of the BOD test.

SUMMARY AND CONCLUSIONS FOR BOD DATA

The data derived from the study of Sample Type VII (Water, Oxygen Demand) indicate the following:

1. When BOD dilutions are selected so as to permit satisfactory determinations of the final dissolved oxygen content, there is no significant difference in the reliability of the BOD values obtained from differing dilutions, within the range of 1% to 2%.
2. The expected precision of the BOD test using this synthetic waste is shown to be approximately $\pm 20\%$.
3. When glucose-glutamic acid is used as a synthetic sewage for BOD evaluation, values obtained after 2 and 3 days incubation are substantially as precise as those after 5 days incubation.
4. Further research is needed to clarify the factors influencing the optimum strength of sewage used for seeding the BOD reaction, and the optimum amount of seed to be added to the waste.
5. The oxidation rate constant of the glucose-glutamic acid synthetic sewage is approximately 0.18 and the ultimate BOD value is approximately 215 mg/l.
6. The ultimate oxygen demand of the synthetic sewage used in this study is approximately 70% of that calculated for the pure substances.

Sample Type VII (Water, Oxygen Demand)

Table VII. BOD RESULTS

1% Dilution

2-Day		3-Day	
BOD - mg/l	Lab. no.	BOD - mg/l	Lab. no.
6	11	106	10
94	28	110	17
95	34	112	34
100	19	114	19
102	10	119	32A
103	20	120	12
111	33	124	11
114	18	124	18
115	17	126	22
116	12	131	8
116	21	131	28
117	5	140	1
122	8	140	5
124	31	151	33
124	SEC	153	9
130	24	154	25A
131	15	157	7
133	9	157	21
135	1	161	6
137	25A	164	13
140	29	167	SEC
144	2	170	24
144	6	170	29
146	32C	171	2
147	25B	176	25B
148	3	182	3
172	35	184	35
154	13	185	32C
155	32B	190	23
157	7	194	16
159	23	198	32B
163	16	218	4
172	4	220	26
213	26		
Geom. mean	120	Geom. mean	152
Median	134	Median	157
Geom. stnd. dev.	35	Geom. stnd. dev.	31

Sample Type VII (Water, Oxygen Demand)

Table VIII. BOD RESULTS

1% Dilution

5-Day		7-Day	
BOD - mg/l	Lab. no.	BOD - mg/l	Lab. no.
100	12	120	12
117	19	120	19
125	15	127	15
132	10	128	11
142	20	141	10
147	34	148	20
153	11	161	34
160	29	186	17
165	1	190	1
165	22	194	28
167	17	195	32A
173	7	197	24
178	33	204	21
189	25B	204	22
190	32A	206	33
196	18	211	18
196	21	221	3
197	13	221	13
198	31	221	26
199	25A	224	5
200	8	225	32B
200	24	227	8
204	9	227	9
210	5	227	25A
211	2	231	2
212	26	231	25B
215	3	237	16
223	23	240	23
224	32B	240	31
227	16	241	32C
229	SEC	266	SEC
238	32C	284	6
247	6	284	7
250	28	290	29
259	35	300	35
274	4	333	4
Geom. mean	187	Geom. mean	207
Median	198	Median	221
Geom. stnd. dev.	41	Geom. stnd. dev.	52

Sample Type VII (Water, Oxygen Demand)

Table IX. BOD RESULTS

2% Dilution

2-Day		3-Day	
BOD - mg/l	Lab. no.	BOD - mg/l	Lab. no.
8	11	114	19
95	20	118	34
100	34	121	10
102	33	123	12
105	10	126	18
105	12	131	22
105	19	134	17
108	32A	136	8
109	28	137	33
114	18	141	25A
118	SEC	147	25B
120	8	148	11
123	9	150	2
123	25B	150	5
124	15	150	9
127	25A	152	7
127	31	156	28
128	17	156	35
130	5	159	SEC
130	6	163	1
130	35	166	32A
131	32B	167	32C
132	3	168	14
135	29	170	29
135	32C	170	32B
137	2	176	23
137	24	176	24
142	4	178	3
145	7	179	6
150	23	181	21
153	1	182	4
160	13	182	13
165	21	192	16
166	16	206	26
167	14		
198	26		
Geom. mean	119	Geom. mean	154
Median	129	Median	156
Geom. std. dev.	31	Geom. std. dev.	23

Sample Type VII (Water, Oxygen Demand)

Table X. BOD RESULTS

2% Dilution

5-Day		7-Day	
BOD - mg/l	Lab. no.	BOD - mg/l	Lab. no.
116	19	105	19
120	12	130	20
125	20	132	12
136	10	151	15
136	15	154	11
154	34	159	10
163	11	164	28
165	29	169	25B
167	33	169	34
175	25B	177	25A
176	25A	188	24
181	7	190	33
182	22	196	17
185	1	198	1
185	28	198	7
188	8	200	31
191	21	202	21
192	2	204	22
192	17	204	32A
192	18	208	18
193	14	211	32B
199	31	212	2
200	32A	214	8
200	35	215	9
202	24	216	23
203	5	217	26
205	9	218	5
206	32B	222	13
208	23	224	3
210	13	228	16
212	26	228	35
218	SEC	230	14
219	3	230	29
220	16	233	32C
222	32C	254	SEC
234	6	264	6
235	4	281	4
Geom. mean	184	Geom. mean	196
Median	192	Median	204
Geom. stnd. dev.	31	Geom. stnd. dev.	37

PRECISION OF THE COD

As mentioned earlier, the chemical oxygen demand test as a chemical analytical procedure is not subject to the biological variation inherent in the BOD. The test, however, does not measure the presence of a specific chemical entity, but rather the ability of the dichromate acid mixture to oxidize the organic matter in the sample.

Previous studies have shown that various pure organic compounds exhibit significantly differing oxidizability in the dichromate test. Thus the "correct" COD cannot be arbitrarily stated, but must be obtained from laboratory data. Therefore, as in the case of the BOD, the correct value for the COD sample is that value most frequently reported by the participating laboratories.

The data is arrayed in Table XII and the mean, median, and standard deviation are shown. From these statistical values, and the appearance of the bar chart in Figure II it is apparent that the distribution is slightly skewed to the left or lower side. The amount of skewness, however, may be considered insignificant.

The standard deviation shown, $\pm 8\%$ of the mean value, is markedly less than that exhibited by the BOD. It is comparable to the precision obtained in other titrimetric methods used in water analysis.

A review of the possible sources of error in the dichromate procedure may explain in part the variation found in this study.

1. The accuracy and precision of the test are affected by the conditions of the reflux step. While the glucose-glutamic acid mixture used as the sample is known to oxidize rapidly under the conditions of the test, mechanical losses during refluxing or transfer of the sample may lead to low results.
2. Since a blank determination is required, essentially two COD determinations must be made, increasing the possible error of the procedure.
3. The titrant used in the test loses strength with time, requiring frequent restandardization. Failure to restandardize produces positive errors.

Sample Type VII (Water, Oxygen Demand)

USE OF COD/BOD RATIO

In spite of the possible errors in the test procedure the demonstrated analytical superiority of the COD suggests its use as a control test for the evaluation of BOD technique. To utilize the COD as a control, it is necessary to obtain the ratio of COD to 5 day BOD and to use this ratio as a test of the BOD technique. In order to demonstrate the use of the ratio, the 5 day BOD values within $\pm 10\%$ of the geometric mean are tabulated in Table XI, along with the corresponding COD's and the ratio of the two values. The mean ratio for the group is 1.49, the median is 1.50, and the values range from 1.22 to 1.82. These data would indicate that a laboratory performing the standard COD and seeded BOD tests on a sample composed of 150 mg/l each of glucose and glutamic acid should obtain a ratio of approximately 1.5 to demonstrate satisfactory performance of the BOD test. Ratios below 1.2 and above 1.8 would indicate unsatisfactory BOD technique.

COMPARISON OF COD WITH THEORETICAL OXIDATION

While no absolute value for COD is available, it is possible to compare the COD values obtained in this study with the theoretical oxygen demand obtained by assuming complete oxidation of the sample to carbon dioxide, water, and nitrogen. For this sample the value was 308 mg/l. The COD values ranged from 68% to 103% of this theoretical value. The mean was 92%.

SUMMARY AND CONCLUSIONS FOR COD DATA

On the basis of the 32 COD values submitted, the following conclusions are drawn:

1. The precision of the test is approximately $\pm 8\%$ of the accepted COD value.
2. Sources of error in the procedure, in addition to the usual manipulative errors, are varying conditions in the reflux step and the necessity for back titration.
3. Since the COD test is more precise than the BOD and is not influenced by seed variables, it is possible to use the ratio of the two values obtained on a standard sample, as an evaluation of BOD performance. A ratio of approximately 1.5 is indicated for the glucose-glutamic acid sample.
4. The COD values varied from 68% to 103% of the theoretical oxygen demand, with a mean of 92%.

Sample Type VII (Water, Oxygen Demand)

CHYANNA, ATAO, WAO, JIN, LANT

Table XI. COD/BOD RATIO

5-day BOD	COD	Ratio
172	210	1.22
174	317	1.82
175	287	1.64
177	265	1.50
180	282	1.57
183	317	1.73
193	257	1.33
193	301	1.56
194	291	1.50
195	291	1.50
198	265	1.34
201	259	1.29
202	296	1.47
203	298	1.47
206	281	1.36
Mean		1.49
Median		1.50
Range		1.22 - 1.82

Sample Type VII (Water, Oxygen Demand)

TableXII. COD DATA ARRAYED

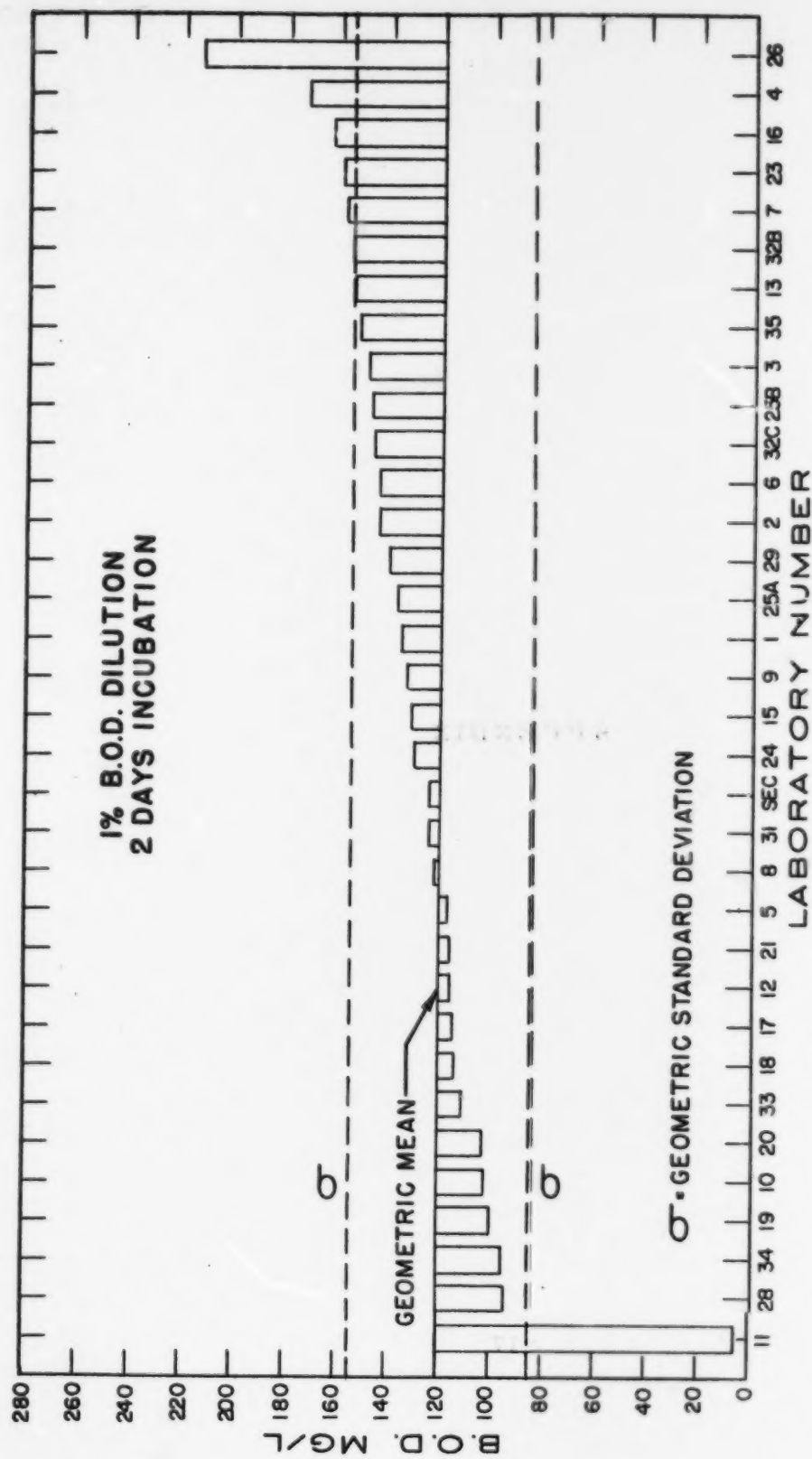
COD - mg/l	Lab. no.	COD - mg/l	Lab. no.
210	33	290	16
243	12	290	3
250	28	291	18
253	35	293	4
254	34	294	27
257	21	295	29
259	24	296	2
265	7	296	SEC
265	31	297	30
271	23	298	13
278	11	299	6
279	15	299	9
281	5	301	14
282	17	305	32A
282	20	317	22
287	1	317	25
289	10		

Mean 281

Median 289

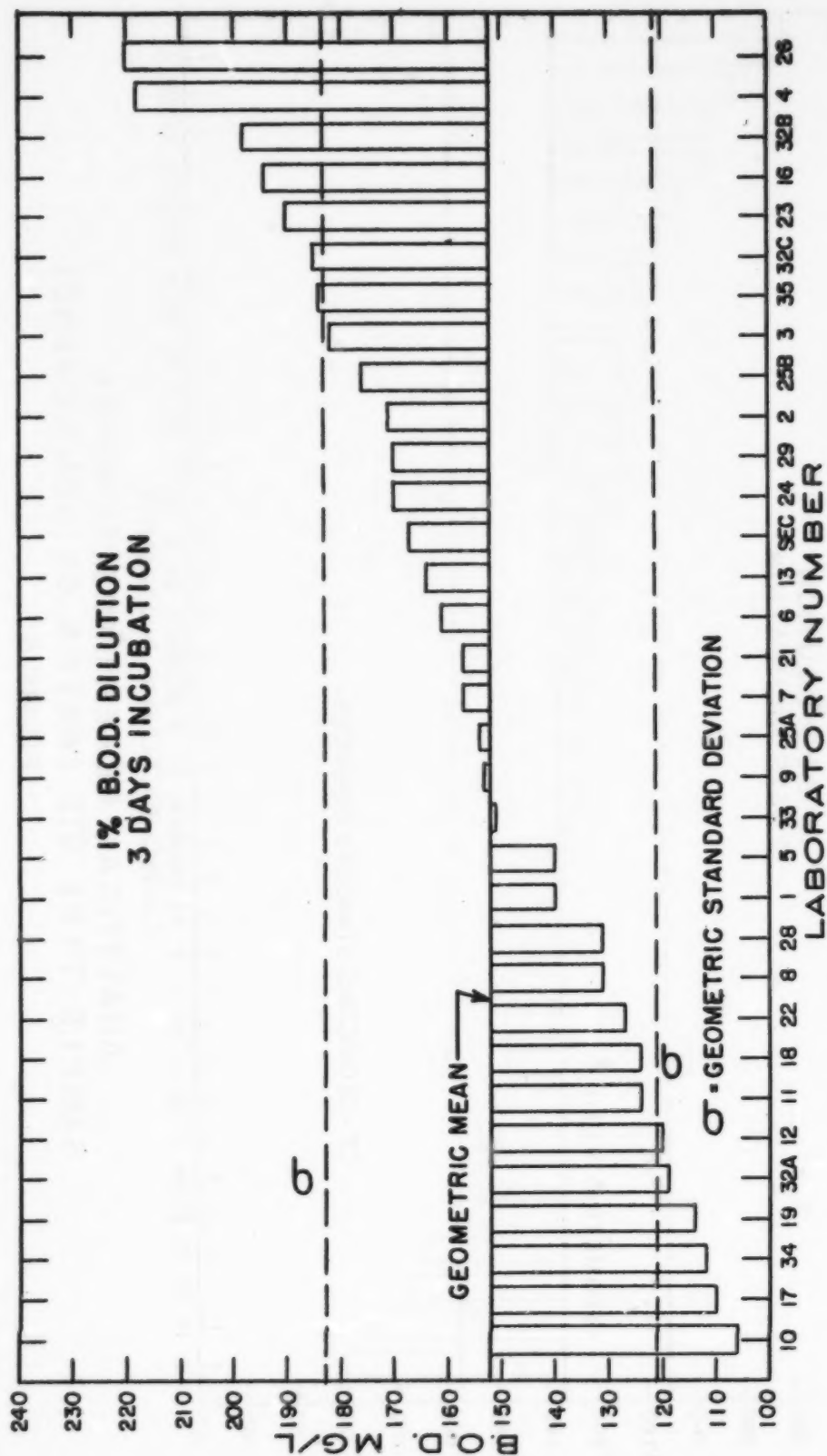
Standard deviation ± 23 (8.2%)

APPENDIX



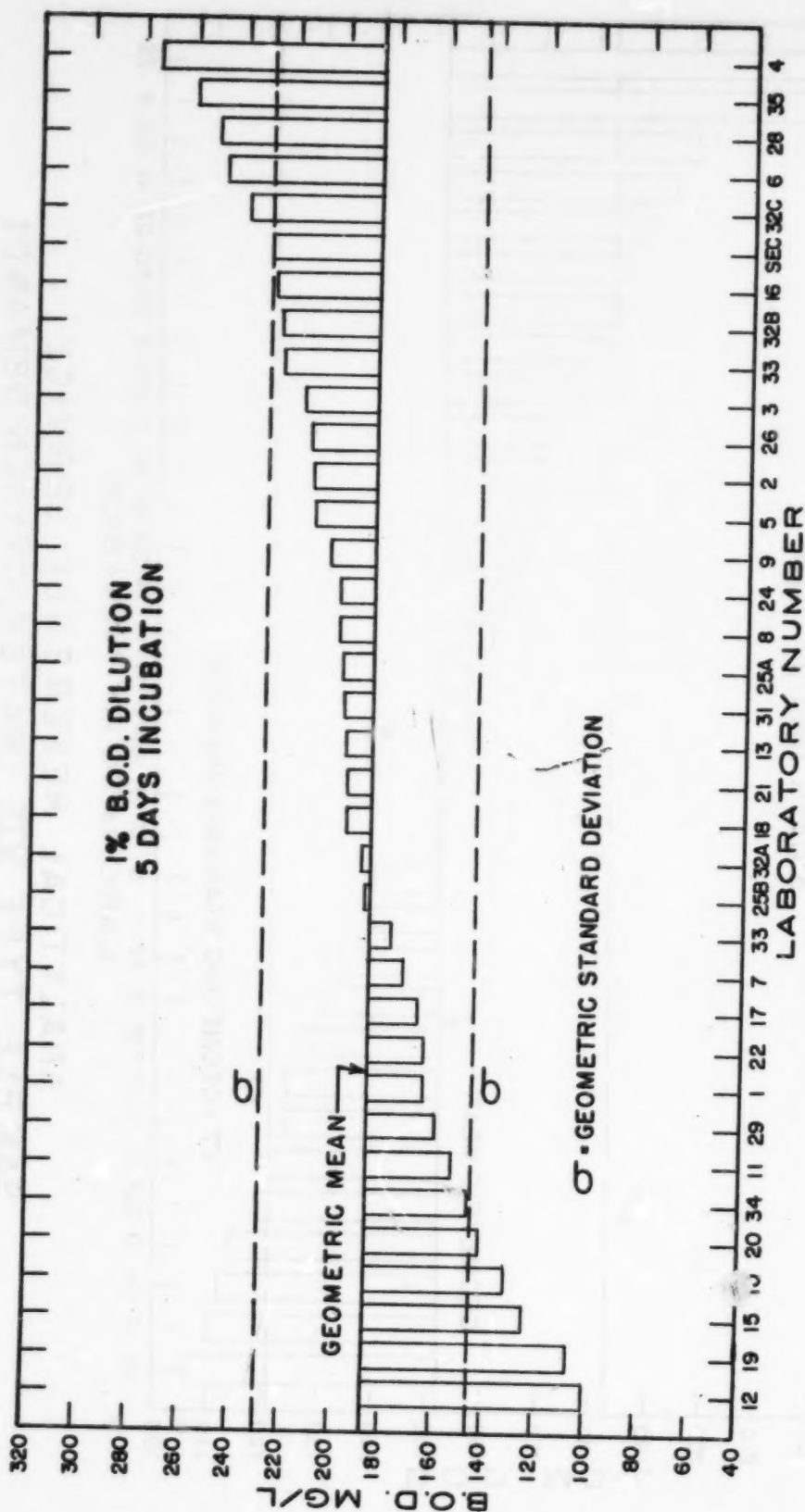
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 1

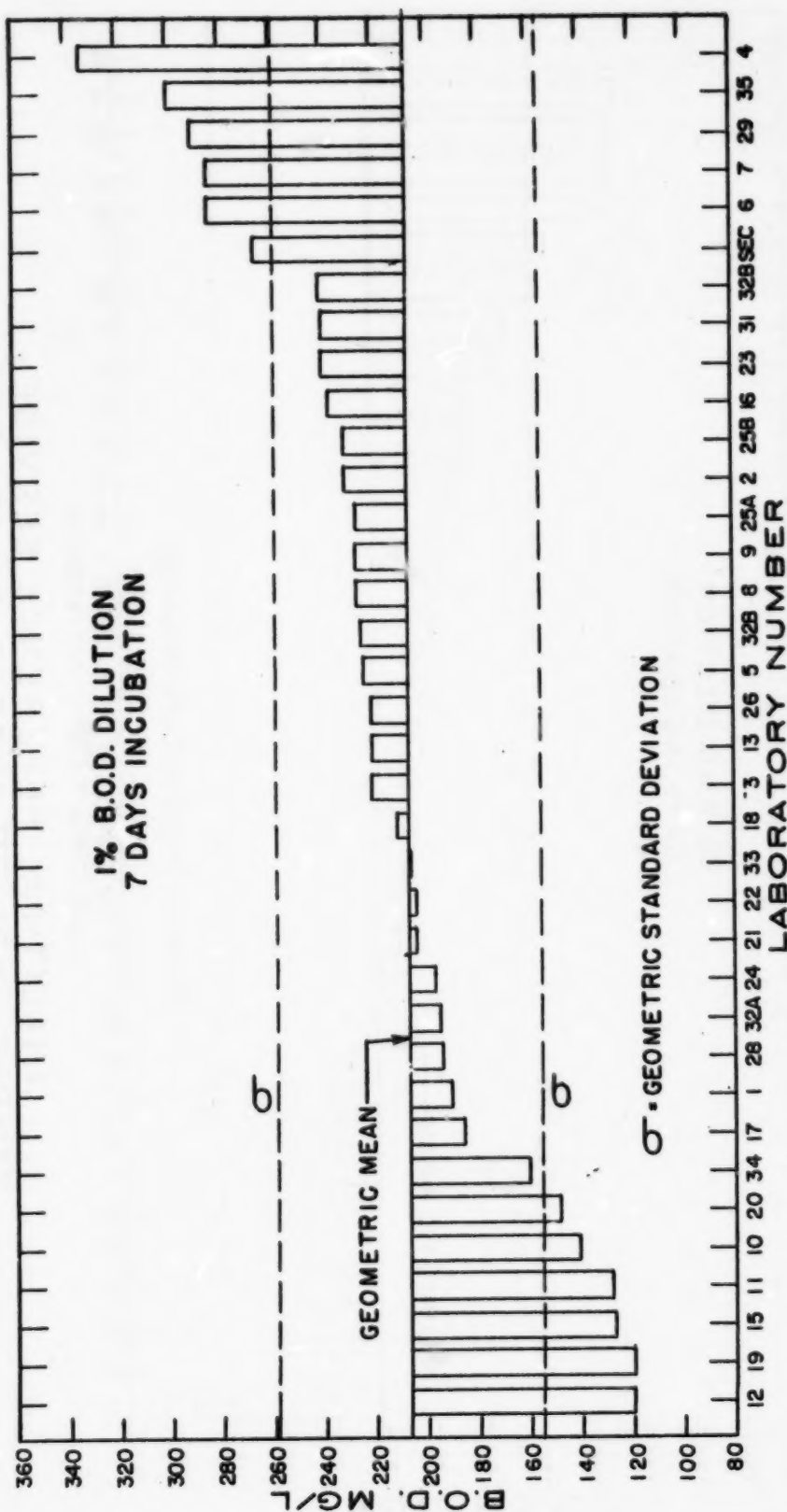


ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 2

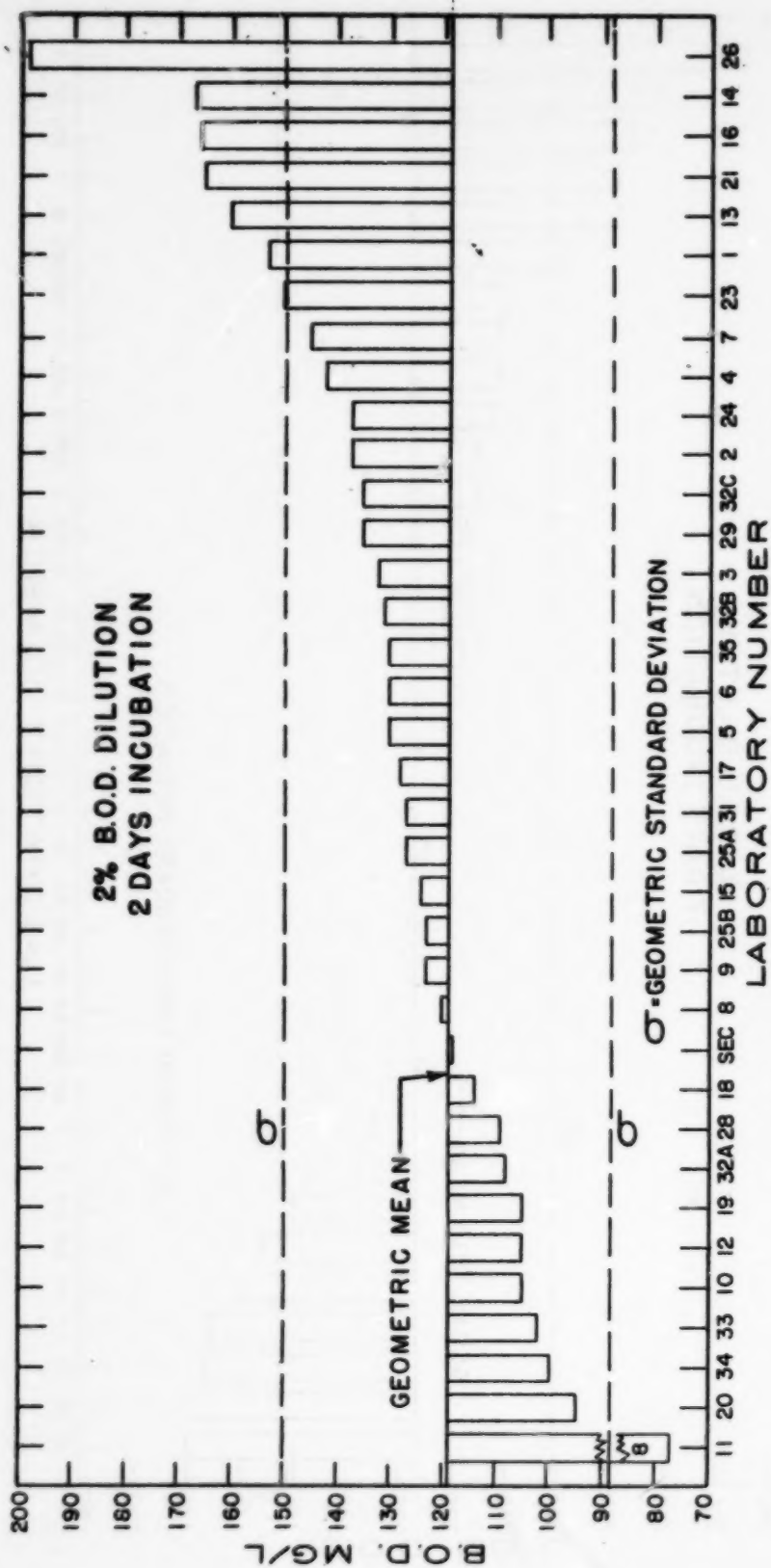


ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)
FIGURE 3



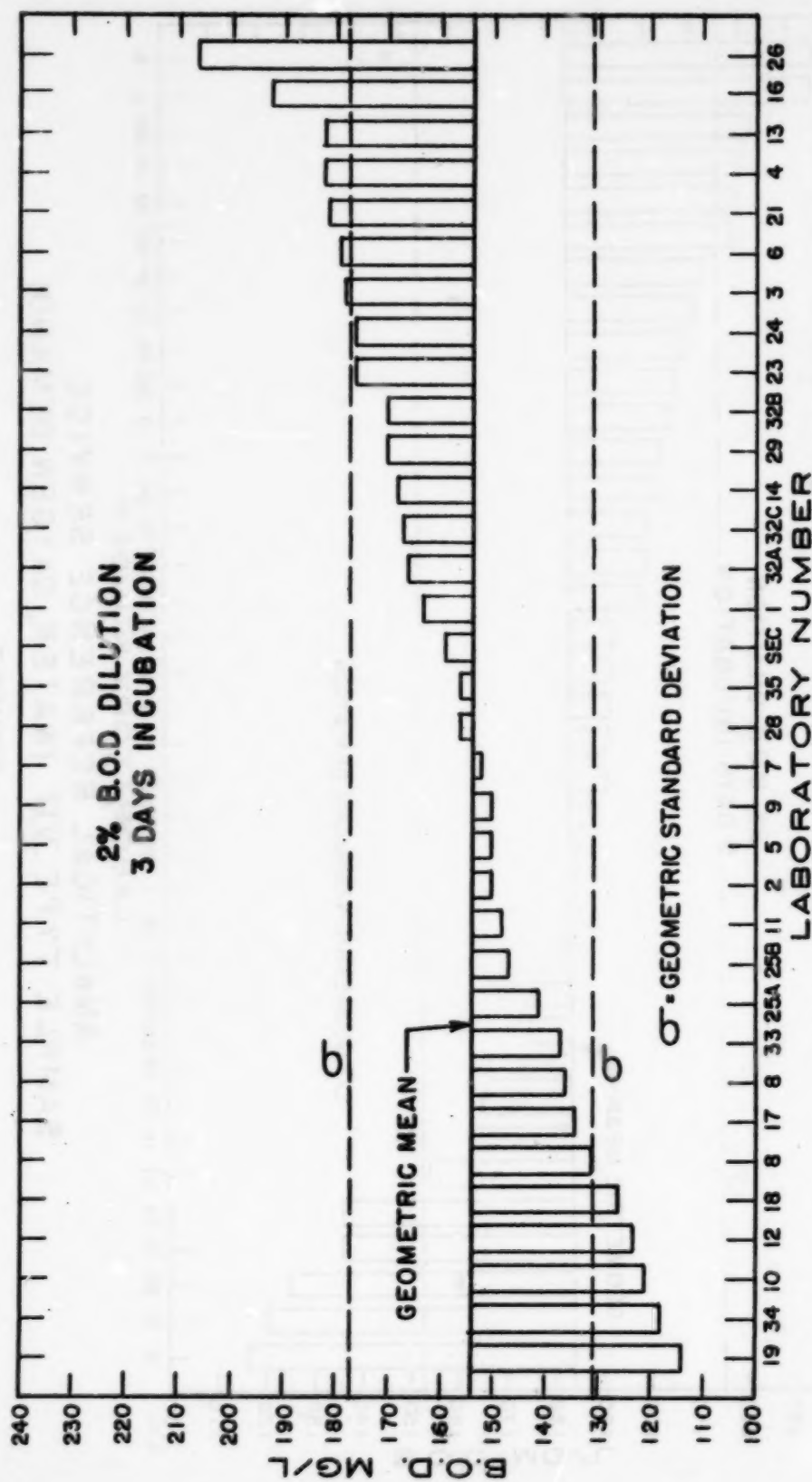
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 4



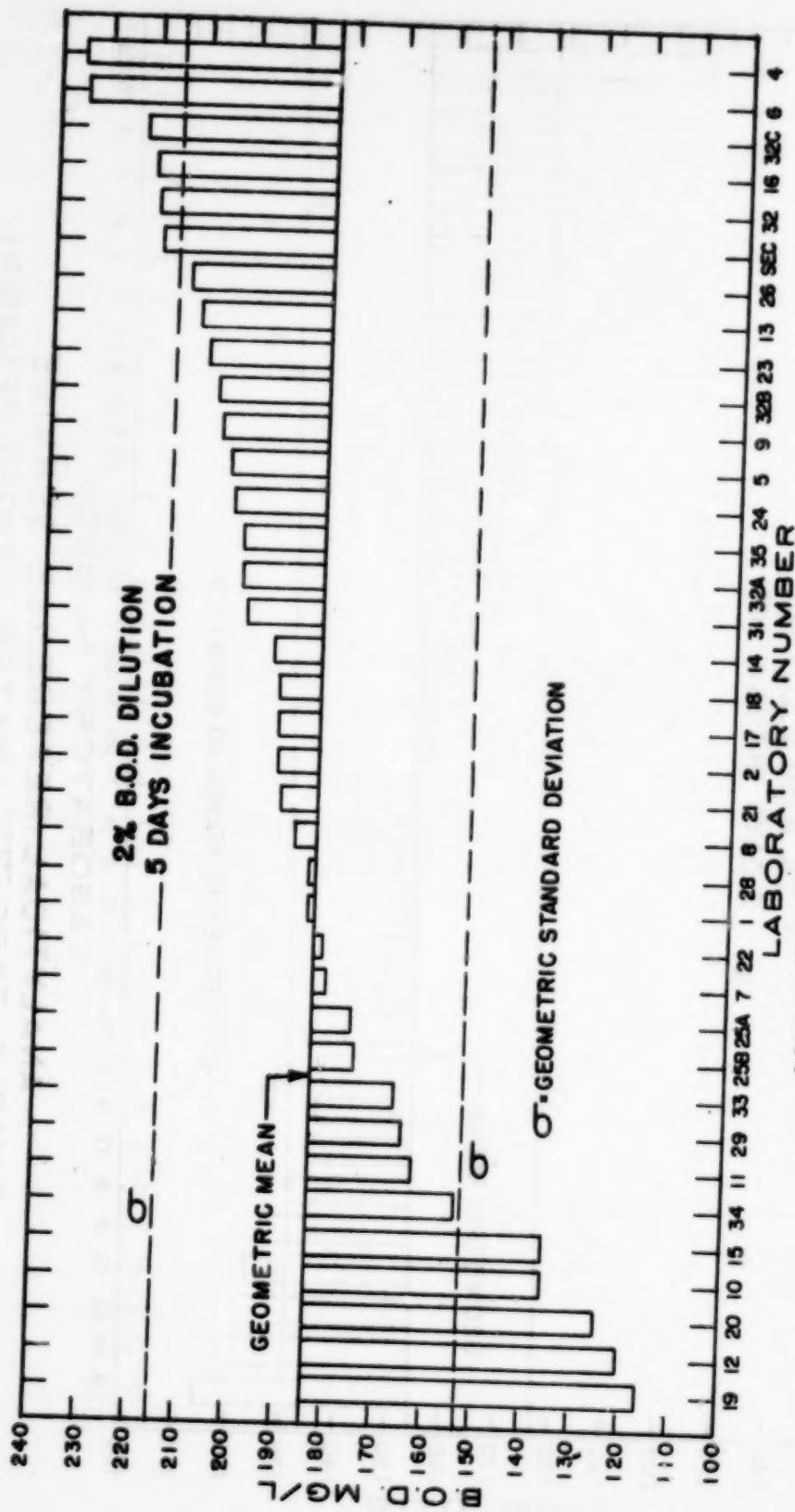
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 5



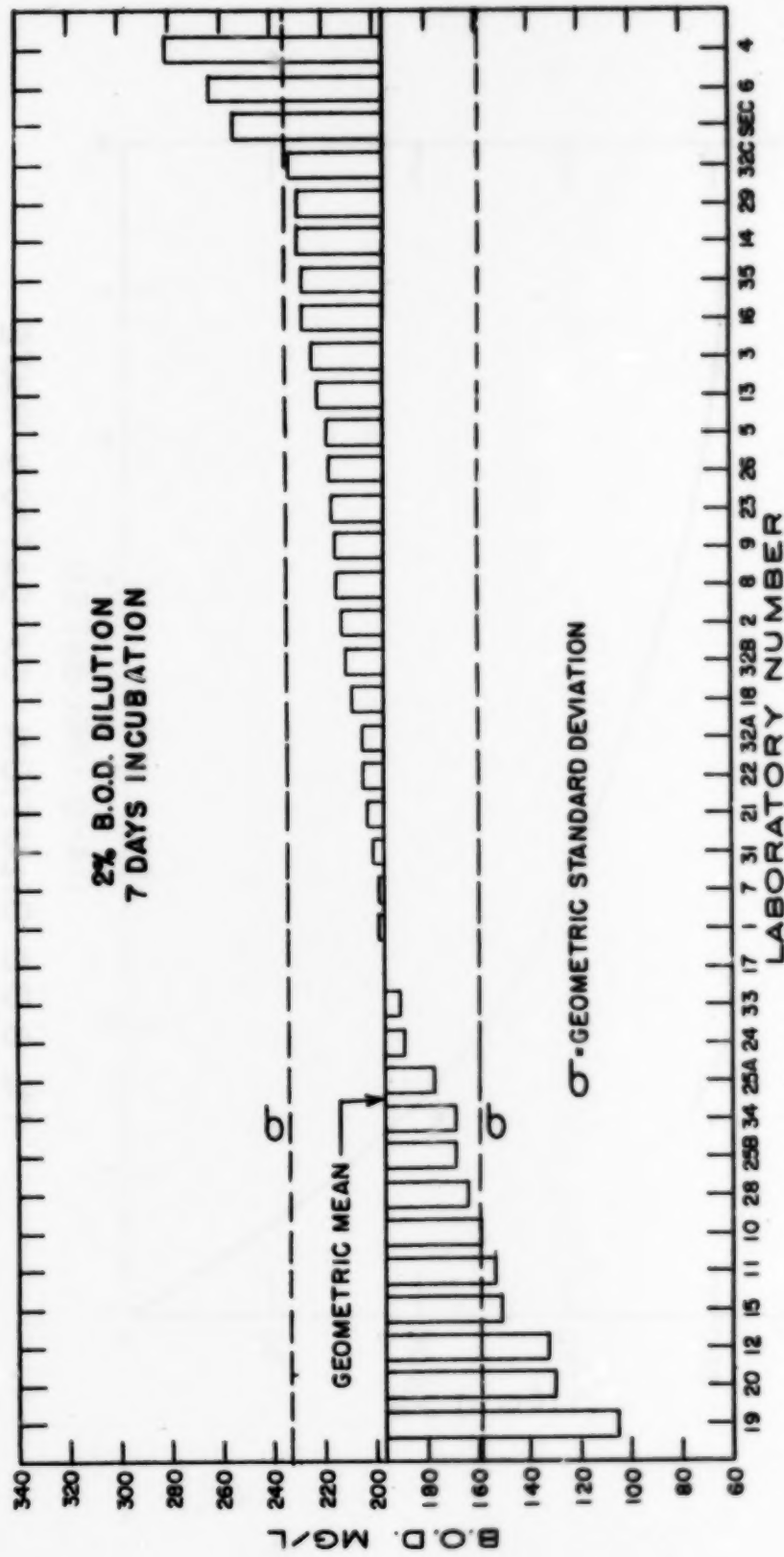
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 6



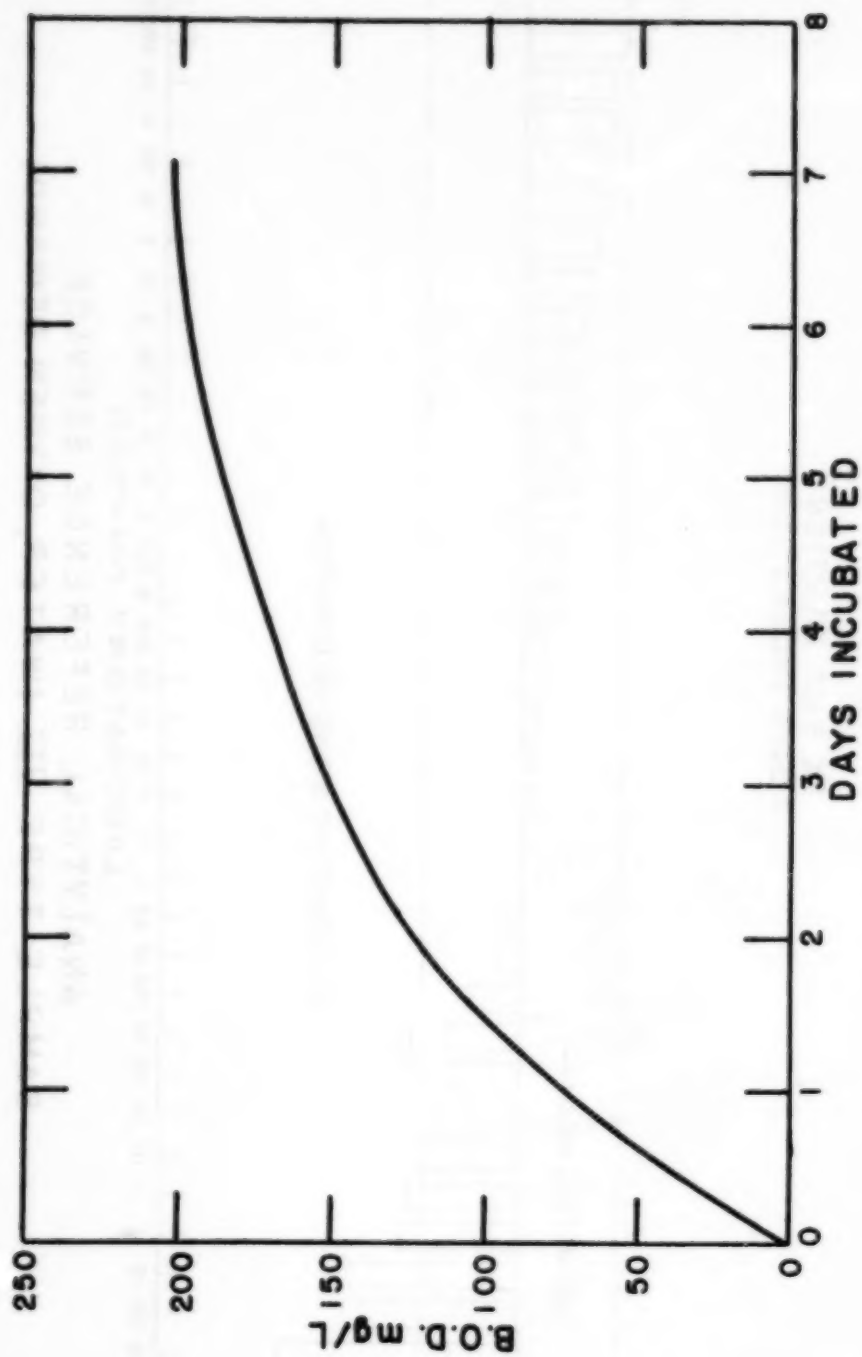
ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)

FIGURE 7



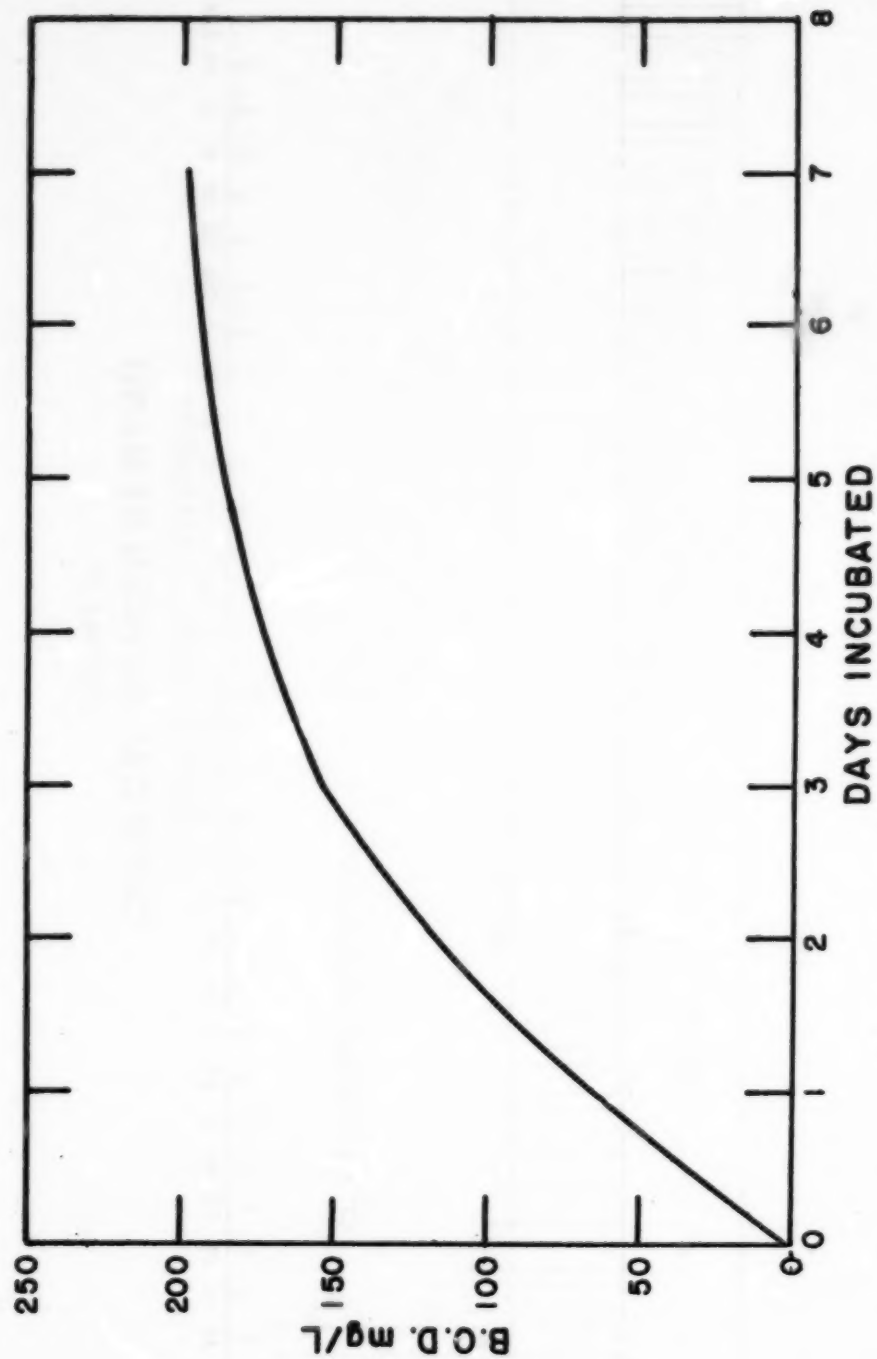
**ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE VII (WATER, OXYGEN DEMAND)**

FIGURE 8



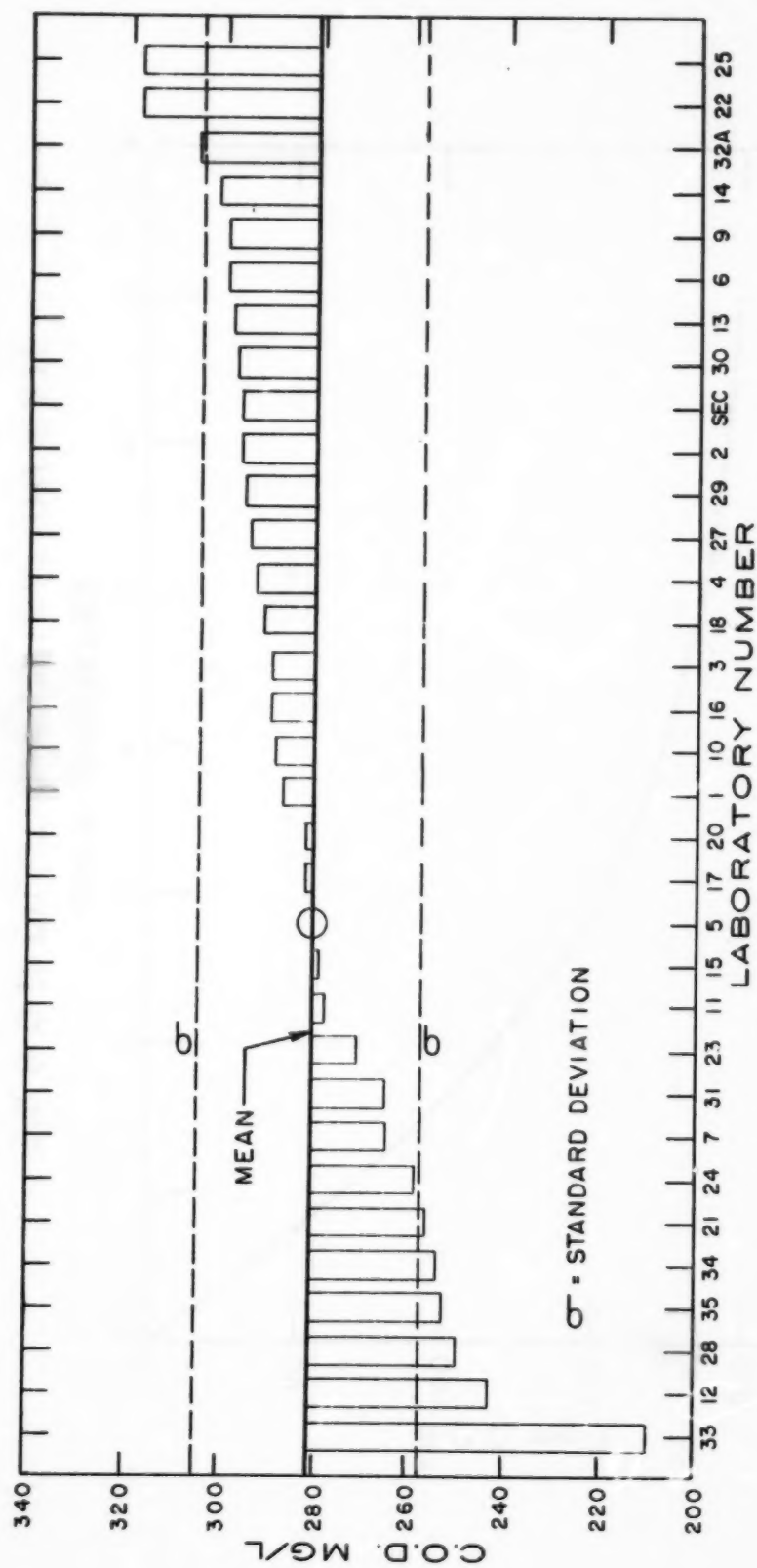
1% B.O.D. DILUTION - OXIDATION RATE

FIGURE 9



2% B.O.D. DILUTION-OXIDATION RATE

FIGURE 10



CHEMICAL OXYGEN DEMAND

FIGURE II